Materials Science-Poland, Vol. 24, No. 1, 2006

Novel composite polymer-in-salt electrolytes based on a PVdF matrix obtained with a solvent-free technique

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Polymer-in-salt electrolytes have been widely investigated as potentially interesting materials for applications in both lithium devices and for basic studies of materials being halfway between polymeric electrolytes and conductive inorganic glasses. Novel composite "polymer-in-salt" electrolytes were synthesized based on a poly(vinylidene difluoride) matrix and various lithium salts. The polymer was chosen due to its high chemical, electrochemical, and thermal stability, widely known from the application in gel electrolytes in lithium batteries. On the other hand, it is well known that a solvent, once incorporated into a PVdF structure, is impossible to remove. Thus a novel method, based on thermal sintering of the composite, was developed to avoid contamination of the sample. Electrolytes of different polymer-to-salt molar ratios, varying from 0.5:1 to 2:1, were synthesized. The influence of preparation conditions (sintering time, temperature and the number of sintering cycles) was also examined. Impedance spectroscopy was used to measure electrical conductivity. Infrared spectroscopy was introduced to investigate ion–ion and ion–polymer interactions and the phase structure of the polymer matrix. Additionally, X-ray diffractometry was applied in structural studies.

Key words: *polymer-in-salt electrolyte; electrical conductivity; composite; ion interactions; lithium*

1. Introduction

Polymer-in-salt electrolytes have been extensively studied in recent years [1–4]. The mechanism of conductivity in these systems is intermediate between that of composite polymeric electrolytes and inorganic ionic glasses. On one hand, the highly conductive region is located on the salt grain boundaries; the observed highly defective structure of the particle surface is similar to that observed in inorganic glassy superconductors. On the other hand, the polymeric material included in these compos-

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ite acts mainly as a binding agent and as a source and stabilizer of the grain surface defects, thus it does not directly take part in charge carrier transport. Percolation between the surface layers of the salt grains must be observed in order to maintain the high mobility paths along the sample, thus a particular minimal volume fraction of the salt in the composite is needed to obtain high conductivity.

The (vinylidene difluoride)-hexafluoropropylene copolymer (Kynar®) matrix has been widely used in gel electrolytes for lithium batteries. The material is known to be chemically, electrochemically, and thermally stable. It is also well known that if a solvent is incorporated into the PVdF structure it is almost impossible to remove it completely [5, 6]. Thus, a typical method of obtaining polymer-in-salt electrolytes based on dissolving the polymer and salt in the solvent, casting the film, and solvent evaporation is unusable when a dry system is taken into consideration.

A thermal method based on the subsequent homogenisation of the polymer and salt mixture, pressing the pellet, and thermal sintering was used to obtain the composites. During the process, temperature was elevated slightly above the melting temperature of PVdF to allow interaction between the salt and matrix. Samples with different sintering times (0.5–12 h) and varying numbers of sintering cycles (1–6) were prepared for various system compositions (salt-to-polymer molar ratios from 0.5:1 to 2:1), for lithium salts including lithium tetrafluoroborate, lithium triflate, LiTFSi, and other lithium salts.

2. Experimental

All the reagents were carefully dried under vacuum (10^{-5} torr, 60 h) prior to use. The drying temperature was in the range 130–160 ºC. The homogenisation process was performed in a nitrogen-filled dry-box with humidity lower than 5 ppm. The pressing process was performed in a steel pan with a working diameter of 13 mm under vacuum (10^{-1}–10^{-2} Torr). The applied load varied with the salt used and was equal to 6000 kg for lithium triflate and 8000 kg for other salts. All the intermittent operations, such as loading of the pan and oven, were also performed in the dry-box. For the sintering process, a vacuum oven made of titanium was used to avoid chemical interaction with the samples. PTFE separators were used on both sides of the sintered pellet. The temperature of the process was equal to 175 ºC and was controlled by a PID regulator. When multi-cycle sintering was performed, the repeated cycle consisted of two hours of sintering in 175 ºC, followed by one hour of cooling to a final temperature of about 120 ºC. For the thermal regime used, not only melting of the crystalline polymer phase was expected (needed for composite formation) but also the phase transition of the PVdF matrix form the α to the β phase.

The sintered pellet used for impedance measurements was covered with a thin gold film by vacuum evaporation to maintain good electrical contact with the test electrodes. The ac impedance was recorded with Atlas 98 HI equipment in the 1 Hz – 100 kHz range for varying temperatures (25–95 ºC). The data obtained were analysed

with Bernard Boukamp's EQ program [7] in order to determine the dc conductivity of the samples. FT-IR measurements of the composites were performed in the Nujol suspension on NaCl plates on a Perkin-Elmer 2000 spectrometer with the resolution of 0.5 cm^{-1}. X-ray diffraction was recorded on a DRON 2 apparatus utilizing CuK_α irradiation with 26 kV and a 16 mA tube current.

3. Results

Impedance spectroscopy measurements show that the dc conductivity of the obtained composites is rather low; at ambient temperature lies in the range 10^{-9} S/cm (Table 1). The differences observed between samples with various compositions and various preparation methods cannot be easily correlated and are not very large. Surprisingly, the expected percolation threshold for samples of higher than 1.25:1 salt-to-polymer ratio, leading to a strong conductivity increase, is also not observed. An exemplary thermal behaviour of conductivity is shown in Figure 1. An Arrhenius-type dependence can be observed for most of the systems studied.

Table 1. Conductivity data for various composite PVdF:salt samples

Sample composition (molar ratio)	Conductivity at 45 °C [S/cm]	Conductivity at 95 °C [S/cm]	Activation energy [kJ/mol]
$LiBF_4$:PVdF, 0.5:1, 2 h	9.19×10^{-10}	5.57×10^{-09}	72.52
$LiBF_4$:PVdF, 0.5:1, 2 h	1.09×10^{-09}	5.35×10^{-09}	79.64
$LiBF_4$:PVdF, 1:1, 0.5 h	3.04×10^{-10}	2.38×10^{-08}	91.52
$LiBF_4$:PVdF, 1:1, 1 h	1.64×10^{-10}	2.28×10^{-08}	102.88
$LiBF_4$:PVdF, 1:1, 1.5 h	1.98×10^{-10}	2.21×10^{-08}	85.95
$LiBF_4$:PVdF, 1:1, 2 h	3.1×10^{-10}	3.3×10^{-08}	99.33
$LiBF_4$:PVdF, 1:1, 6 h	1.01×10^{-09}	1.03×10^{-08}	87.18
$LiBF_4$:PVdF, 1:1, 8 h	1.54×10^{-08}	1.54×10^{-08}	89.21
$LiBF_4$:PVdF, 1:1, 12 h	3.5×10^{-10}	1.56×10^{-08}	94.03
$LiBF_4$:PVdF, 1.5:1, 2 h	3.18×10^{-09}	9.18×10^{-09}	99.85
$LiCF_3SO_3$:PVdF, 1:1, 2 h	2.7×10^{-10}	5.02×10^{-10}	14.32
$LiCF_3SO_3$: PVdF, 1:1, 6 h	2.21×10^{-10}	4.97×10^{-10}	17.67
$LiCF_3SO_3$: PVdF, 0.5:1, 2 h	1.68×10^{-10}	4.68×10^{-10}	19.32
$LiCF_3SO_3$: PVdF, 1.5:1, 2 h	6.06×10^{-11}	4.82×10^{-10}	15.87
$LiAlCl_4$:PVdF, 0.5:1, 2h	2.92×10^{-10}	5.46×10^{-09}	59.98
LiNTFS:PVdF, 0.5:1, 2 h	1.68×10^{-10}	4.68×10^{-10}	34.45
LiNTFS:PVdF, 1:1, 2 h	1.48×10^{-10}	1.14×10^{-08}	82.04
LiNTFS:PVdF, 1.25:1, 2 h	3.50×10^{-09}	1.73×10^{-08}	43.53
$LiAsF_6$:PVdF, 1.5:1, 2h	1.22×10^{-10}	1.67×10^{-09}	52.21
$LiPF_6$:PVdF, 1.5:1, 2 h	1.11×10^{-10}	6.2×10^{-09}	77.05
$LiPF_6$:PVdF, 2:1, 2 h	9.51×10^{-10}	7.14×10^{-07}	93.80

Judging from the FT-IR spectra (Fig. 2), there is no evidence of Li^+ cation coordination by polymer chains in PVdF–$LiCF_3SO_3$ composites for any studied salt-to-

polymer molar ratios (i.e. from 1:2 to 1:0.5). The positions of the characteristic salt peaks in the spectra of composite samples are almost the same as in the spectrum of pure salt. The only observed difference is in the intensity of the higher frequency contribution (with a maximum at ~658 cm^{-1}) of the peak ascribed to δ_s SO_3. In the spectrum of the crystalline salt, the maximum of this peak was found at 652 cm^{-1}, whereas in the spectra of the composite sample with a high (above 1:1) salt-to-polymer molar ratio a splitting of this band was observed.

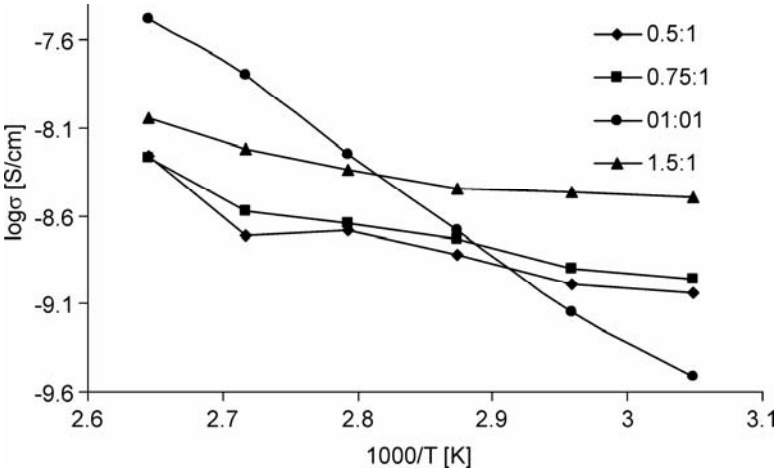

Fig. 1. Thermal dependence of conductivity for PVdF:$LiBF_4$ samples with different compositions

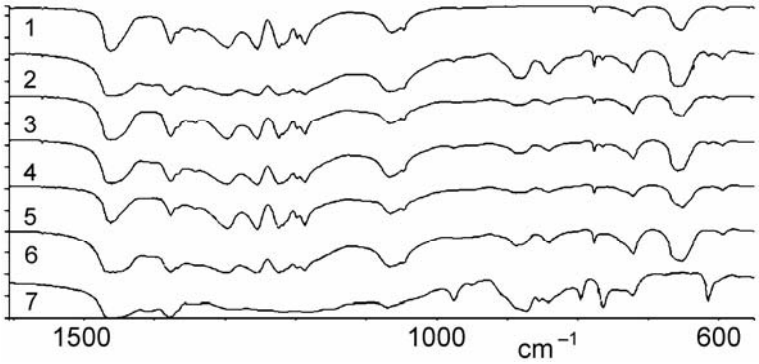

Fig. 2. FT-IR spectra of PVdF–$LiCF_3SO_3$ composites for varying salt-to-polymer molar ratios (2 – 1.5:1, 3 – 1.25:1, 4 – 1.0:1, 5 – 0.75:1, 6 – 0.5:1) compared to pure salt (1) and pure polymer (7)

We found bands ascribed both to the crystalline and amorphous phases in the spectrum of the polymer [8, 9]. It should be noticed that in the spectrum of the pure polymer mostly bands characteristic of the so-called α-phase appear, while in the composite samples we found peaks of the β-phase and of the amorphous phase of the polymer. For example, in the spectrum of PVdF powder we observed strong peaks at

795 and 615 cm^{-1}, due to t_{CH_2} and δ_{CF_2} of the α-phase. On the other hand, two various signals at 873 and 841 cm^{-1} indicate the presence of the β-phase. In the spectra of polymer electrolytes, the bands of the α-phase disappear and new spectral features at 888 cm^{-1} can be observed. All bands become broader, which may indicate a more amorphous structure.

Similar changes in the polymer characteristic pattern can be observed in the spectra of the PVdF–LiTFSI composites (Fig. 3). As in the case of $LiCF_3SO_3$-based electrolytes, the positions of the bands of the salt in the composite samples are close to those of the crystalline salt and not to those of a "free" anion. The interpretation of the spectra of PVdF–$LiBF_4$ electrolytes is more difficult, because of their poor quality. The trend observed was essentially the same, i.e. the transition of PVdF from the α to β phase in the composite samples, a result of their thermal history.

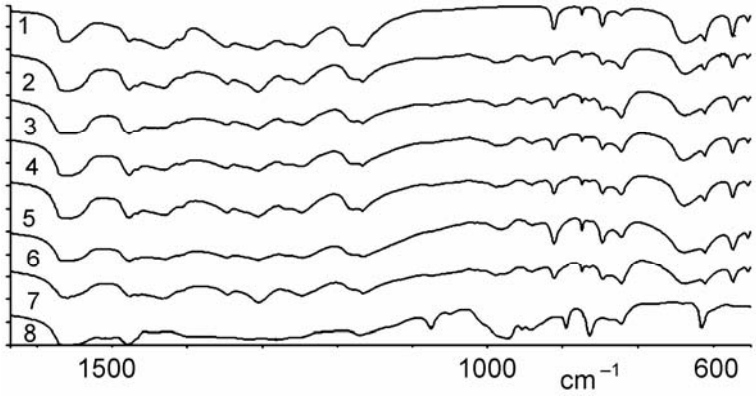

Fig. 3. FT-IR spectra of PVdF-LiTFSi composites for varying salt-to-polymer molar ratios (2 – 0.5:1, 3 – 0.75:1, 4 – 1:1, 5 – 1.25:1, 6 – 1.5:1, 7 – 2.0:1) compared to pure salt (1) and pure polymer (8)

It has to be stressed, however, that the conducting properties of solid electrolytes can be strongly affected by the type and content of the crystalline phases as well as by the distribution of the salt in the polymer matrix. We plan to perform a more detailed study of "polymer-in-salt" electrolyte structure by means of Raman mapping.

XRD experiments were first performed for pellets made of pure salts. All the compounds used were tested. A comparison between the diffraction images recorded for sintered and non-sintered pellets reveals no important differences in either reflex position or their intensity. Thus, it can be claimed that neither phase transition nor material degradation is observed under conditions identical to those used for further composite synthesis. In the second step, a set of pellets made of pure polymer matrix was investigated (Fig. 4). In this case, a recrystallisation process can be observed when comparing data for the pristine pellet (a) to those registered for the one sintered at 160 ºC, i.e. below the melting temperature of the crystalline phase. The intensity of reflex increases and the half-width decreases (Table 2), pointing not only to an in-

crease of the amount of crystalline phase, but also to an increase in crystallite size. For a partially melted sample (c, 170 ºC), a loss of crystallinity is observed. The most

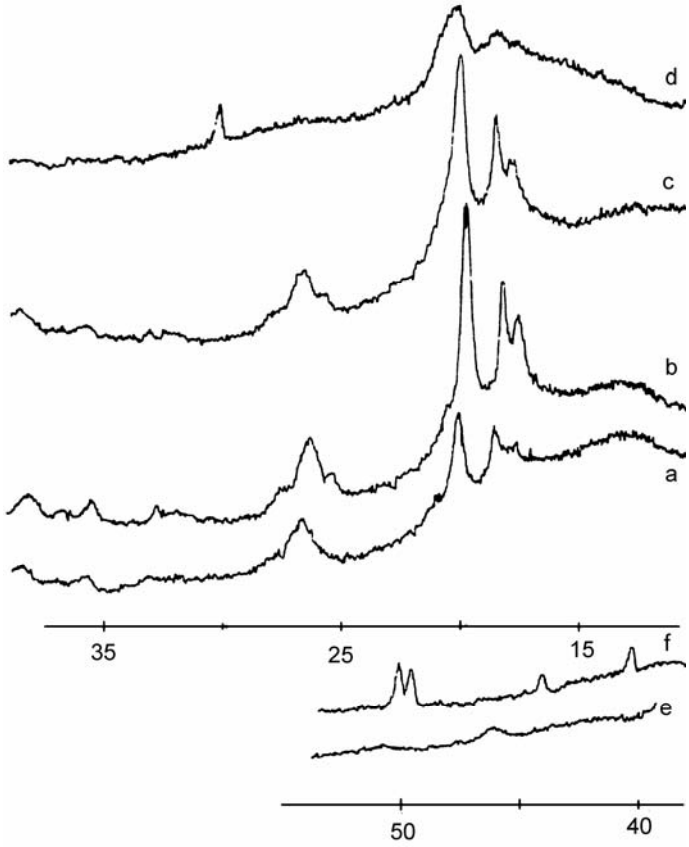

Fig. 4. X-ray diffraction patterns for PVdF pellets; a) pressed, b, e) sintered at 160 ºC, c) partially melted at 170 ºC, d, f) fully melted at 175 ºC

interesting changes are observed for the fully melted sample (d, 175 ºC) – not only does the crystallinity significantly decrease, but also a new phase is observed. The change in the shapes and positions of the peaks around $2\theta = 20^{\circ}$ is in agreement with literature data [9]. Additionally, new reflexes at about 40º and 50º can be observed, proving β phase generation. Finally, composite samples containing $LiBF_4$ were tested. The diffraction image reveals reflexes only from the salt phase. No traces of crystallinity for the polymer matrix were observed, even for the sample with the lowest salt content. These data contradict those obtained from FT-IR experiments. This discrepancy can be easily explained considering the fact that FT-IR collects information from all crystallites independent of their size, while XRD is sensitive only to objects with sizes above a particular threshold. The composite sample can contain a crystalline PVdF phase (mainly β), but in the form of very small regions.

Table 2. X-ray diffraction data collected for pure PVdF samples with different thermal histories

Sample	2Θ	Reflex intensity
PVdF, 160 ºC	17°30′ 18°15′ 19°45′ 26°25′	124 180 390 207
PVdF, 170 ºC	17°45′ 18°30′ 20°00; 26 °40′	116 156 320 180
PVdF, 175 ºC	20°7′ 30°10′ 40°20′ 44°10′ 49°50′ 50°20′	275 48 40 28 64 78
PVdF, 200 ºC	17°35′ 18°30′ 20°5′ 26°45′	12 72 68 170

Acknowledgements

The authors would like to thank all their co-workers from the research group for help, comments and valuable discussions. The State Committee for Scientific Research is kindly acknowledged for financial support of the presented research under grant No. 134/E-365/S/2004.

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Received 10 December 2004
Revised 18 March 2005